(19) Japan Patent Office (JP) (12) **Patent Notification** (A)

(11) Patent application publication No. **Patent No. 63-256427**

(43) Published on 24-10-1988

(51) Int.Cl.[4]	Identification sign	Int. Ref. No.
B29 D 11/00		6660-4F
B29 B 9/10		6804-4F
C08 J 3/12	CFJ	Z-8115-4F
B29 K71:00		

Investigation request: Not applied No. of inventions 1 (Pages 6)

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(54) Title of the invention: Method of production of optical elements

(21) Application No. Sho 62-91144 (22) Published on 14-4-1987

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Details

1.Title of the invention

Production of optical element

2. Claim

Method of production of optical elements prepared by fused molding of a resin composition obtained by first dissolving a resin composition consisting of a polymeric portion mainly containing aromatic vinyl monomer and polyphenylene ether portion, followed by removing the foreign particles by filtration of the solution obtained by dissolving the composition in an organic solvent and then removing the organic solvent by passing it through an extrusion type pelletization machine having a vent in it.

3. Detailed description of the invention

Fields of industrial usage

This invention is concerned with optical elements that is, it is concerned with optical disk substrate for optically recording and reproducing information and for lenses and prisms.

Conventional techniques

U.S.P 473065 has reported optical elements made from polymer originating from organic vinyl monomer and plyphenylene ether.

To be specific, the above patent has reported optical disk substrate made from a mixture of polystyrene and polyphenylene ether.

In Patent JP61-221225, method of production of polycarbonate resin in which a mixture of water and polycarbonate resin is kneaded and extruded while allowing the gas to escape, has been mentioned.

The problems this invention sought to solve

Optical elements are required to have good dimensional stability and low double refraction and especially for optical disks, this demand is very severe, the C/N ratio of recording and replay has to be sufficiently high and the bit error has to be low.

Further, in case of other optical elements like lenses and prisms also, resin material like methacrylate resin is used but there is a demand for optical elements originating from resins with low double refraction, good thermal resistance and having lesser foreign particles.

Over the years, efforts for producing the substrate of erasable and re-writable optical magnetic disks from plastic are going on.

In optical disks, while reading the recorded information, polarized laser ray is allowed to fall on the recorded medium by focusing by means of a lens, and the information is read by detecting the minute rotation of polarized reflected laser due to Karr effect. For this, it is necessary to use a disk substrate, which does not allow double refraction even for a beam incident obliquely.

Further, since the substrate gets heated during writing, the optical disk should have high thermal resistance.

Optical disk substrate made from a polymer portion mainly composed of aromatic vinyl monomer and polyphenylene ester portion has low double refraction, high thermal resistance and it is not hygroscopic and thus it has good dimensional stability. It also does not deform easily but the C/N ratio is not sufficiently high and it still cannot be considered for reliable substrate for optical disk.

The present invention has taken this into consideration and thus its aim is to present optical elements obtained by injection molding or compression molding with following features. Low double refraction, low double refraction even in case of a beam incident obliquely, high thermal resistance, good balance of mechanical strength, excellent

dimensional stability, being perfectly uniform, without any macro and micro composition distribution, having lesser number of particles of foreign matter and having high performance and high reliability.

Procedure for solving the problems

This invention is concerned with the method of production of optical elements obtained by fused molding of a resin composition obtained by first dissolving a resin composition consisting of a polymeric portion mainly containing aromatic vinyl monomer and polyphenylene ether portion, followed by removing the foreign particles by filtration of the solution obtained by dissolving the composition in an organic solvent and then removing the organic solvent by passing it through an extrusion type pelletization machine having a vent in it.

The resin composition of this invention consists of a mixture of a polymer mainly composed of aromatic vinyl monomer and polyphenylene ether, a block polymer or graft polymer made from a polymer mainly composed of aromatic vinyl monomer and polyphenylene ether components or their mixture.

Examples of polymer mainly composed of aromatic vinyl monomer are, polymer of aromatic vinyl monomer or a copolymer containing at least 50 weight % of aromatic vinyl monomer. Examples of aromatic vinyl monomer are styrene, α-methyl styrene, m-methyl styrene, p-methyl styrene, o-chloro-styrene, m-chloro-styrene, p-chloro-styrene, m-bromo-styrene, p-bromo-styrene. However, styrene is desirable.

Examples of monomers copolymerizing with aromatic vinyl monomer are: unsaturated nitriles like acrylonitrile, methacrylonitrile; methacrylate esters like methyl methacrylate, n-propyl methacrylate, iso-propyl methacrylate, n-butyl methacrylate, cyclohexyl methacrylate; alkyl acrylates like methyl acrylate, propyl acrylate and butyl acrylate. Moreover, methacrylic acid, acrylic acid, maleic anhydride, citraconic acid anhydride, N-methyl maleimide, N-phenylmaleimide can also be used.

These copolimerizable monomers can be used independently or by mixing. However, the copolymer with aromatic vinyl monomer and the resin composition made from this copolymer and polyphenylene ether are combined in such a way that they do not hinder.

It is better that the proportion of the aromatic vinyl monomer in the homopolymer is at least 50-weight %. If it is less than 50 weight %, the resin thus obtained becomes hygroscopic and it is undesirable.

The fused fluidity (melt flow rate, MFR) of the polymer mainly consisting of aromatic vinyl monomer at 230°C at 3.8 kg load is 0.5 ~ 200 but desirable value of this is 2 ~ 100.

If this value is more than 200, the mechanical strength gets affected and if it is less than 0.5, it reduces the double refraction.

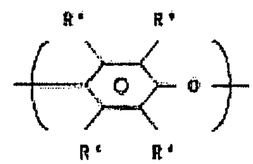
Any method like block polymerization, suspension polymerization emulsion polymerization or solution polymerization can be used for the preparation of polymer mainly containing aromatic vinyl monomer, by radical initialization. However, block polymerization or suspension polymerization is better from the point of productivity and avoiding the mixing of foreign particles.

Peroxides like lauryl peroxide, benzoyl peroxide, di-tertiarybutyl peroxide, di-cumyl peroxide; azo-compounds like 2,2'-azobis-isobutylonitrile, 1,1'-azobis (1-cyclohexane carbonitrile) can be used as radical initiators.

Further, for adjusting the molecular weight, tert-butyl, n-butyl, n-octyl, n-dodecyl and tert-dodecyl mercaptan can be added, if necessary, as chain transfer agents.

The polymerization is carried out usually at a temperature in the range 50 ~ 150°C.

The polyphenylene ether used in this invention is a polymer containing repeated units expressed by the general formula



(Where, R^a, R^b, R^c and R^d represent hydrogen or hydrocarbon group).

The polyphenylene ether is a polymer obtained by oxidative coupling of a phenol monomer. It can be easily obtained by the method mentioned in patents JP36-18692, JP47-36518, JP48-17396, JP49-16120, JP57-44625, JP57-147517, JP58-19329, JP58-19330 and JP58-122919.

Specific examples of this polyphenylene ether are poly (2,6-dimethyl-1,4-phenylene) ether, poly (2-methyl-6-ethyl-1,4-phenylene) ether, poly (2-methyl-6-propyl-1,4-phenylene) ether, poly (2,6-dipropyl-1,4-phenylene) ether and poly (2-methyl-6-bromo-1,4-phenylene) ether. However, poly (2,6-dimethyl-1,4-phenylene) is desirable.

The polymers that are usually used as engineering plastics can be used as polyphenylene ether and the one with lower molecular weight is preferable.

The block copolymer or graft copolymer composed of a polymer mainly consisting of aromatic vinyl monomer portion and polyphenylene ether portion can be obtained by polymerizing a monomer in presence of the other polymer.

Specific examples of this method are those mentioned in patents JP42-22069, JP47-1210, JP47-47862 and JP52-38596. In this block or graft polymerization, a monomer mainly consisting of aromatic vinyl monomer is polymerized in presence of polyphenlene ether.

Alternatively, a phenol monomer is polymerized by oxidative coupling in presence of a polymer mainly consisting of aromatic vinyl monomer.

The proportion of polymer mainly containing aromatic vinyl monomer and polyphenylene ether portion is such that the former is 30 ~ 70 weight % and desirably 40 ~ 55 weight % and the latter is 30 ~ 70 weight % and desirably 45 ~ 60 weight %.

If the polyphenylene ether portion is less than 40 weight% or if it exceeds 70 weight %, the double refraction of the optical element does not reduce sufficiently. If it is less than 40 weight %, the thermal resistance also becomes insufficient.

The resin composition can be selected in the above range.

In this invention, examples of organic solvents are benzene, toluene, xylene and chloroform but toluene and xylene are desirable.

In this invention, solvent means the one in which the resin composition dissolves completely in molecular order.

The dissolution is carried out at a pressure prevailing at the time of dissolution and at a temperature below the boiling point, and desirable pressure is atmospheric pressure. Thus the dissolution is carried out at a temperature below the boiling point of the solvent at the atmospheric pressure.

Further, the resin composition made from polymer portion mainly consisting of aromatic vinyl monomer and polyphenylene ether portion per 100 parts by weight is at least 1 part by weight and up to 100 parts by weight. The desirable value is from 3 parts by weight to 75 parts by weight and still desirable value is from 5 parts by weight to 50 parts by weight. However, the weight of resin composition to be dissolved is selected according to the organic solvent temperature and pressure at the time of dissolution in such a way that a uniform solution is obtained.

For removing foreign particles of size 1 μm or more, the solution is filtered in advance.

The filter used for filtering should be able to remove fine particles of size 1 μm or more. For this purpose, filter paper, pulp, sintered metal filter, metal fiber or ceramic filter can be used.

For removing fine foreign particles, batch methods like pressurized filtration, vacuum filtration or, continuous filtration can be used but continuous filtration is desirable.

Desirable temperature for filtration is the one at which the viscosity during filtration is up to 1 poise and desirably up to 100 centipoises and still desirably up to 50 centipoises.

After removal of the foreign particles, the solution can be fed to the screw injection molding machine as such, but it is fed to the injection molding machine by concentrating by flash evaporation so that the resin composition per 100 parts by weigh of the solution becomes at least 5 parts by weight, desirably at least 10 parts by weight and still desirably at least 10 parts by weight.

For removing the solvent while extruding by screw extrusion machine, at least one vent is provided at the reduced pressure up to 500 mm Hg, desirably up to 400 mmHg and still desirably up to 200 mmHg.

The operational temperature is such that passage through the screw should be smooth.

Evaporation time is an essential condition for deciding the vent pressure, operational temperature and the quantity of solvent remaining in the resin composition after the pelletization.

The quantity of solvent remaining in 100 parts of the resin composition is up to 0.5 parts by weight, desirably up to 0.3 parts by weight and still desirably 0.1 parts by weight.

The operational conditions are adjusted by trial, so as to keep the residual solvent as stated above.

Stabilizers for synthetic resin, like stereo-hindered phenol, organic phosphite, and organic phosphates can be added to the solution being fed to the screw extrusion machine.

In this invention, 'fused molding' means conducting molding when the resin is in flowing condition, above its glass transition temperature.

The methods like injection molding, extrusion molding or compression molding can be mentioned.

The molding temperature is 35 °C above the glass transition temperature.

All the processes after this are carried out in dust free atmosphere.

Application examples

'Parts' and '%' in application examples are on the basis of weight.

Measurement of properties and processing operations in the application examples were as follows.

Double refraction: Retardation was measured at 546 nm by using polarized microscope by using Senarmon compensator method.

Optical transmittance: Automatic intensity meter (Manufactured by Hitachi, Model 330) was used and optical transmittance of a sample of 1.2 mm thickness was measured at 800 nm.

Water absorption: Equilibrium average water absorption was measured at 60°C in distilled water on the basis of ASTM D-570.

Thermal resistance: Mentioned in terms of glass transition temperature by means of linear expansion coefficient method.

Limiting viscosity of polymer: Ubbelohde viscometer was used and measurement and calculation was done in chloroform solution at 25°C.

C/N ratio: Measurement was done by means of Hewlett-Packard Spectrum Analyser-835A scanning optical system, under the conditions of 30 KHz band width of scanning filter.

Pit error rate:
Recording conditions:
Rotation speed: 1800 rpm
Recording frequency: 3 MHz
Duty: 50%
Recording power: 6 mW
Recording magnetic field: 3500 e

Under the above conditions, 300 track (10 seconds) recording was carried out and the proportion of period of signal-missing portion on reproducing at 1 mW power was considered as bit error rate. The above measurements were conducted at radius of 40, 45, 50 and 55 and their average was considered as pit error rate.

Mixing-kneading and pelletization were carried out by using a biaxial screw extruder with 2 vents (Manufactured by Nippon Steel Industries Model TEX 30-30BW-2V).

Injection molding was carried out by using Neomat 150/75 (75 ton) model Manufactured by Sumitomo Heavy Industries. The mold used was for molding a disk of130 mm diameter and 1.2 mm thickness.

Method of production of optical magnetic disk: Silicon reactive spattering was carried out on the substrate obtained thus by injection molding in an atmosphere of a mixture of argon and nitrogen at reduced pressure of 5×10^{-3} Torr and a silicon nitride film of thickness 850 Å having double refraction of 2.0 was created.

Then on this, a magnetic layer of Tb Fe Co of 900 Å was prepared by the usual method and then an optical disk having 850 Å silicon nitride substrate /silicon nitride/TbFeCo/silicon nitride structure was prepared.

Application example 1

Poly (2,6-dimethyl-1,4-phenylene) ether of limiting viscosity 0.40 (in chloroform, 25°C) was prepared by the method mentioned in application example 2, No. 9 of Patent JP47-36518 by polymerizing 2,6-xylenol by using manganese chloride and ethanolamine as catalysts.

10 kg of resin composition containing 50 parts of this polyphenylene ether and 50 parts of Esprite 4-62-A (Sumitomo Chemical Industries) as polystyrene was dissolved uniformly in 100 liters of toluene at 80°C.

While maintaining this solution at 80°C, it was filtered through a membrane filter of diameter 145 mm and pore size 2 μm at a pressure 0.5 kg/cm^2 and again filtered through a membrane filter of diameter 145 mm and pore size 0.45 μm at a pressure 0.5 kg/cm^2.

The solution thus obtained as above, by removing foreign particles was fed to a biaxial extruder with its cylinder temperature set at 260°C and by reducing the vent pressure to 100 mmHg and pelletization was carried out while distilling out the solvent.

All the processes after this were carried out in dust free atmosphere.

These pellets were injection molded at cylinder temperature 300°C and mold temperature 110°C to get optical disk substrate of 130 mm diameter and 1.2 mm thickness.

The optical transparency of this substrate disk was 86 % and double refraction at 35 mm from the center of the circular plate was +1 nm, moisture absorbance was 0.1%, glass transition temperature was 145°C and number of foreign particles was 2330 particles/g.

The C/N value of optical magnetic disk was 45 dB. Further, the pit error was 7.7×10^{-5}.

Comparison example 1

The procedure was as in application example 1 except that filtration was omitted.

The optical transparency of this substrate disk was 86 % and double refraction at 35 mm from the center of the circular plate was +1 nm, moisture absorbance was 0.1%, glass transition temperature was 145°C and number of foreign particles was 325360 particles/g.

The C/N value of optical magnetic disk was 45 dB. Further, the pit error was 4.1×10^{-4}.

Comparison example 2

50 parts of polyphenylene ether used in application example 1 and 50 parts of Esprite 4-62A (as polystyrene) were mixed and mixed, pelletized by means of a biaxial screw extrusion machine and disk substrate was prepared.

Optical transparency of the disk substrate thus obtained was 86%, its double refraction at 35 mm position from the center of the disk was +1 nm, water absorption was 0.1 %, glass transition temperature was 145°C and number of foreign particles were 343480 /g.
C/N ratio of the optical disk was 40 dB and pit error ratio was 3.2×10^{-4} .

Effect of this invention

By this invention the foreign particles are reduced to an extremely small number and therefore, high performance, high reliability optical elements can be obtained.

Especially the number of fine foreign particles in case of optical elements, made from polymer portion mainly containing aromatic vinyl monomer and polypenylene ether, is extremely small and thus an extremely uniform blending is obtained. This gives an optically highly isotropic and highly thermally resistant, highly efficient and highly reliable optical element.

The optical elements of this invention are suitable for substrate of optical disk, lenses, optical cards and prisms.

As stated above, when used for optical disk, because of its low double refraction and high thermal resistance, it shows good properties and sufficiently high recording and reproduction C/N ratio and sufficiently small pit error rate.